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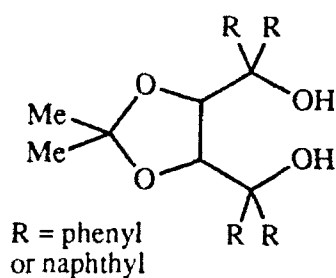
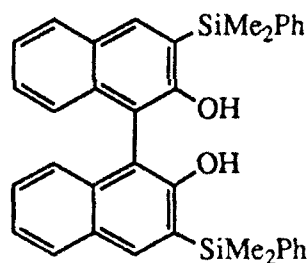
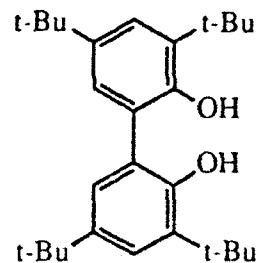
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**Abstract**

Well-defined molybdenum ROMP catalysts that contain C<sub>2</sub>-symmetric diolate ligands (tartrates, binaphtholates, or biphenolates) have been prepared and shown to polymerize 2,3-R<sub>2</sub>norbornadienes (R = CF<sub>3</sub> or CO<sub>2</sub>Me) to give, in the most favorable case, >99% cis polymers that are >99% tactic.

Controlling the stereochemistry of polymers prepared by ring-opening of norbornenes and norbornadienes has been a long standing problem,<sup>1,2</sup> one that ultimately could be solved by employing well-characterized catalysts with known structures and activities. Catalysts of the type  $\text{Mo}(\text{CH-t-Bu})(\text{NAr})(\text{OR})_2$  ( $\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-i-Pr}_2$ )<sup>3,4</sup> have been shown to ring-open polymerize 2,3-bis(trifluoromethyl)norbornadiene (NBDF6) to give highly tactic all-trans polyNBDF6 when  $\text{OR} = \text{O-t-Bu}$  (in toluene or THF)<sup>5</sup> and all-cis polyNBDF6 with a tactic bias of ~74% when  $\text{OR} = \text{OCMe}(\text{CF}_3)_2$  (in THF).<sup>6</sup> We show here that catalysts of this general type can be prepared that contain  $\text{C}_2$ -symmetric chiral diolate ligands and that poly-2,3-bis(trifluoromethyl)norbornadiene (polyNBDF6) and poly-2,3-dicarbomethoxynorbornadiene (polyDCNBD) can be prepared using them that are >99% cis and >99% tactic.

C<sub>2</sub>-Symmetric tartrate and BINO derivatives (see below) and related C<sub>2</sub>-symmetric ligands have been widely and successfully used for enantioselective organic reactions in the past

 $R_4\text{tartH}_2$  $\text{BINO}(\text{SiMe}_2\text{Ph})_2\text{H}_2$ 

**Bipheno(t-Bu)<sub>4</sub>H<sub>2</sub>**

decade.<sup>7-20</sup> Addition of (+)-Ph<sub>4</sub>tartH<sub>2</sub> to Mo(CHCMe<sub>2</sub>Ph)(NAr)(OTf)<sub>2</sub>(DME)<sup>21,22</sup> (DME = dimethoxyethane) in diethyl ether in the presence of triethylamine yielded Mo(CHCMe<sub>2</sub>Ph)(NAr)[(+)-Ph<sub>4</sub>tart](S) ((+)-**1**; S = a mixture of NEt<sub>3</sub> and dme; see Supplementary Material) in 70% yield. Mo(CHCMe<sub>2</sub>Ph)(NAr)[(-)-Ph<sub>4</sub>tart](S) ((-)-**1**) and Mo(CHCMe<sub>2</sub>Ph)(NAr)[(+)-Nap<sub>4</sub>tart](S) ((+)-**2**; Nap = β-naphthyl) were prepared in an analogous manner. (±)-BINO(SiMe<sub>2</sub>Ph)<sub>2</sub>H<sub>2</sub> was prepared in a manner analogous to known SiR<sub>3</sub> derivatives<sup>7</sup> and treated with two equivalents of KCH<sub>2</sub>Ph<sup>23</sup> to give (±)-BINO(SiMe<sub>2</sub>Ph)<sub>2</sub>K<sub>2</sub>, which when added to Mo(CH-t-Bu)(NAr)(OTf)<sub>2</sub>(DME)<sup>21,22</sup> in THF gave crystalline Mo(CH-t-

Bu)(NAr)[(±)-BINO(SiMe<sub>2</sub>Ph)<sub>2</sub>](THF) ((±)-3) in 70% yield.<sup>24,25</sup> Crystalline Mo(ChCMe<sub>2</sub>Ph)(NAr')[(±)-BINO(SiMe<sub>2</sub>Ph)<sub>2</sub>](THF) ((±)-4; Ar' = 2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>) was prepared from (±)-BINO(SiMe<sub>2</sub>Ph)<sub>2</sub>K<sub>2</sub> and Mo(ChCMe<sub>2</sub>Ph)(NAr')(OTf)<sub>2</sub>(DME)<sup>26</sup> in a manner analogous to that used to prepare (±)-3. NMR spectra of (+)-1, (-)-1, and (+)-2 show an H<sub>α</sub> and C<sub>α</sub> resonance for a single alkylidene rotamer, while NMR spectra of (±)-3 and (±)-4 suggest that they are mixtures of anti and syn rotamers.<sup>27,28</sup> (See Supplementary Material.)

The cis/trans ratio in polyNBDF6 is determined readily and accurately by <sup>13</sup>C NMR,<sup>5,6</sup> while tacticity can be determined at the triad level by analyzing the resonances for C(7), as shown in Figure 1(a).<sup>6</sup> The resonance at 38.38 ppm in Figure 1(a) can be assigned to C(7) in a tactic polymer (cc,mm or cc,rr triad), while that at 37.61 ppm can be assigned to C(7) in atactic polymer (cc,mr triad).<sup>6</sup> The resonance at 36.44 is assignable to C(7) in a polymer whose tacticity is different than that which gives rise to the C(7) resonance at 38.38 ppm, while the minor broad resonances in Figure 1(a) can be ascribed to C(7) in ct triads.

PolyNBDF6 prepared from (+)-2 in DME (97% cis; Table I) precipitates as it is being formed. The fact that the polymer is relatively insoluble in DME, dichloromethane, toluene, and THF (although soluble in acetone) prevented determination of molecular weight and polydispersity by GPC. The C(7) region of the <sup>13</sup>C NMR spectrum of this polymer in acetone-d<sub>6</sub> (Figure 1(b)) shows primarily one carbon resonance (at 38.31 ppm), consistent with a tacticity of 97% for the all-cis triads (Table I) on the basis of the cc assignments shown in Figure 1(b). PolyNBDF6 prepared from (+)-1 in DME or THF, which was identical to that prepared from (-)-1 in DME or THF, was soluble in THF and had a lower all-cis tacticity (88%; Table I). (A higher enantioselectivity has been observed employing Nap<sub>4</sub>tart as a chiral auxiliary instead of Ph<sub>4</sub>-tart in organic reactions.<sup>14,17</sup>)

PolyNBDF6 prepared using (±)-3 as the initiator in THF is only ~71% cis, although the tacticity of the all-cis triads is relatively high (86%; Table I). However, polyNBDF6 prepared from 200 equiv of NBDF6 and (±)-4 as the initiator was >99% cis and was soluble only in acetone. Its <sup>13</sup>C NMR spectrum in the C(7) region is shown in Figure 1(c). The narrow 38.31

ppm resonance is virtually the only C(7) resonance present. The  $^1\text{H}$  NMR spectrum of this polymer is also relatively sharp and well-resolved. (See Supplementary Material.) Therefore we propose that this polymer is at least 99% tactic. The vastly improved cis/trans ratio and percent tacticity upon changing from isopropyl groups to methyl groups in the imido ligand of the initiator is striking. An oligomer of polyNBDF6 (28 mer) prepared using ( $\pm$ )-**4** is soluble in THF and has a molecular weight (4900 versus polystyrene) and polydispersity (1.09) consistent with a living ROMP polymerization.

In order to test whether tacticity control is possible with other norbornadiene derivatives we prepared samples of poly-2,3-dicarbomethoxynorbornadiene using **1**, **2**, **3**, and **4** as initiators and compared them with polyDCNBD prepared employing  $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$  in  $\text{DME}^4$  as shown in Table II. ( $^{13}\text{C}$  NMR spectra of polyDCNBD are closely analogous to those for polyNBDF6.) The percent tacticity for polyDCNBD was at least as high as that for polyNBDF6 in every case involving a chiral initiator.

Finally, we prepared  $\text{Mo}(\text{CH-t-Bu})(\text{NAr})[\text{Biphen}(\text{t-Bu})_4]$  (**5**) by adding  $\text{Biphen}(\text{t-Bu})_4\text{K}_2$  to  $\text{Mo}(\text{CH-t-Bu})(\text{NAr})(\text{OTf})_2(\text{DME})$  in THF. The  $\text{Biphen}(\text{t-Bu})_4$  ligand has been shown to "flip" rapidly on the NMR time scale in some lanthanide complexes,<sup>29</sup> although it is "locked" on the NMR time scale (300 MHz) in **5** at 25°C. We were somewhat surprised to find that polyDCNBD (250 mer) prepared from **5** in THF was >99% cis and 96% tactic.

We have now proven by proton NMR that all cis polymers prepared from enantiomerically pure dicarboalkoxynorbornadienes are isotactic, while the all trans polymer are syndiotactic.<sup>30</sup> Therefore we believe that the all cis, tactic polymers prepared here are also isotactic, and that a bias toward isotacticity by chain end control using  $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$  as the initiator is being enhanced by site control at a chiral metal center. Future studies will be aimed at determining under what conditions other monomers can be polymerized stereoselectively. One might also consider the possibility that catalysts such as (+)-**1** or (+)-**2**, or enantiomerically pure versions of **3** or **4**, could selectively

polymerize or ring-close<sup>31,32</sup> one enantiomer in a racemic mixture.

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**Table I.** Poly[2,3-bis(trifluoromethyl)norbornadiene]<sup>a</sup>

Catalyst	cis (%)	cis tactic (%)	equiv	M <sub>n</sub> <sup>b</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>	yield (%)
Mo(CHCMe <sub>2</sub> Ph)(NAr)[OCMe(CF <sub>3</sub> ) <sub>2</sub> ] <sup>c</sup>	97	74	100	19 500	1.05	85
Mo(CHCMe <sub>2</sub> Ph)(NAr)[(+)-Ph <sub>4</sub> tar] (+)-1	98	88	100	14 000	1.05	95
Mo(CHCMe <sub>2</sub> Ph)(NAr)[(+)-Nap <sub>4</sub> tar] (+)-2 <sup>d</sup>	97	97	100	-	-	85
Mo(CH-t-Bu)(NAr)[(±)-BINO(SiMe <sub>2</sub> Ph) <sub>2</sub> ] (±)-3	71	86	100	11 200	1.06	87
Mo(CHCMe <sub>2</sub> Ph)(NAr)[(±)-BINO(SiMe <sub>2</sub> Ph) <sub>2</sub> ] (±)-4 <sup>e</sup>	>99	>99	200	-	-	97

<sup>a</sup> All polymers were prepared in THF, unless otherwise noted. <sup>b</sup> Determined by GPC in THF versus polystyrene standards. <sup>c</sup> Prepared as described in reference 6. <sup>d</sup> Prepared in DME. <sup>e</sup> A 28 mer was found to be soluble in THF and had M<sub>n</sub> = 4900 and M<sub>w</sub>/M<sub>n</sub> = 1.09.

**Table II.** Poly[2,3-dicarbomethoxynorbornadiene]<sup>a</sup>

Catalyst	cis (%)	cis tactic (%)	equiv	M <sub>n</sub> <sup>b</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>	yield (%)
Mo(CHCMe <sub>2</sub> Ph)(NAr)[OCMe(CF <sub>3</sub> ) <sub>2</sub> ] <sup>c</sup>	98	73	100	16 400 <sup>d</sup>	1.04 <sup>d</sup>	86
Mo(CHCMe <sub>2</sub> Ph)(NAr)[(+)-Ph <sub>4</sub> tar] (+)-1 <sup>c</sup>	93	93	100	23 000	1.60	85
Mo(CHCMe <sub>2</sub> Ph)(NAr)[(+)-Nap <sub>4</sub> tar] (+)-2	93	97	100	51 500	2.38	80
Mo(CHCMe <sub>3</sub> (NAr)[(±)-BINO(SiMe <sub>2</sub> Ph) <sub>2</sub> ] (±)-3	93	97	100	34 000	1.84	94
Mo(CHCMe <sub>2</sub> Ph)(NAr)[(±)-BINO(SiMe <sub>2</sub> Ph) <sub>2</sub> ] (±)-4	>99	>99	100	28 700 <sup>f</sup>	1.28 <sup>f</sup>	97
Mo(CH-t-Bu)(NAr)[Bipheno(t-Bu) <sub>4</sub> ] 5	>99	96	250	56 000	1.33	95

<sup>a</sup> All polymers were prepared in THF, unless otherwise noted. <sup>b</sup> Determined by GPC in CH<sub>2</sub>Cl<sub>2</sub> versus polystyrene standards. <sup>c</sup> Prepared in DME as described in reference 4. <sup>d</sup> GPC analysis performed in THF. <sup>e</sup> Prepared in DME. <sup>f</sup> Prepared in CH<sub>2</sub>Cl<sub>2</sub>/THF (4:1).

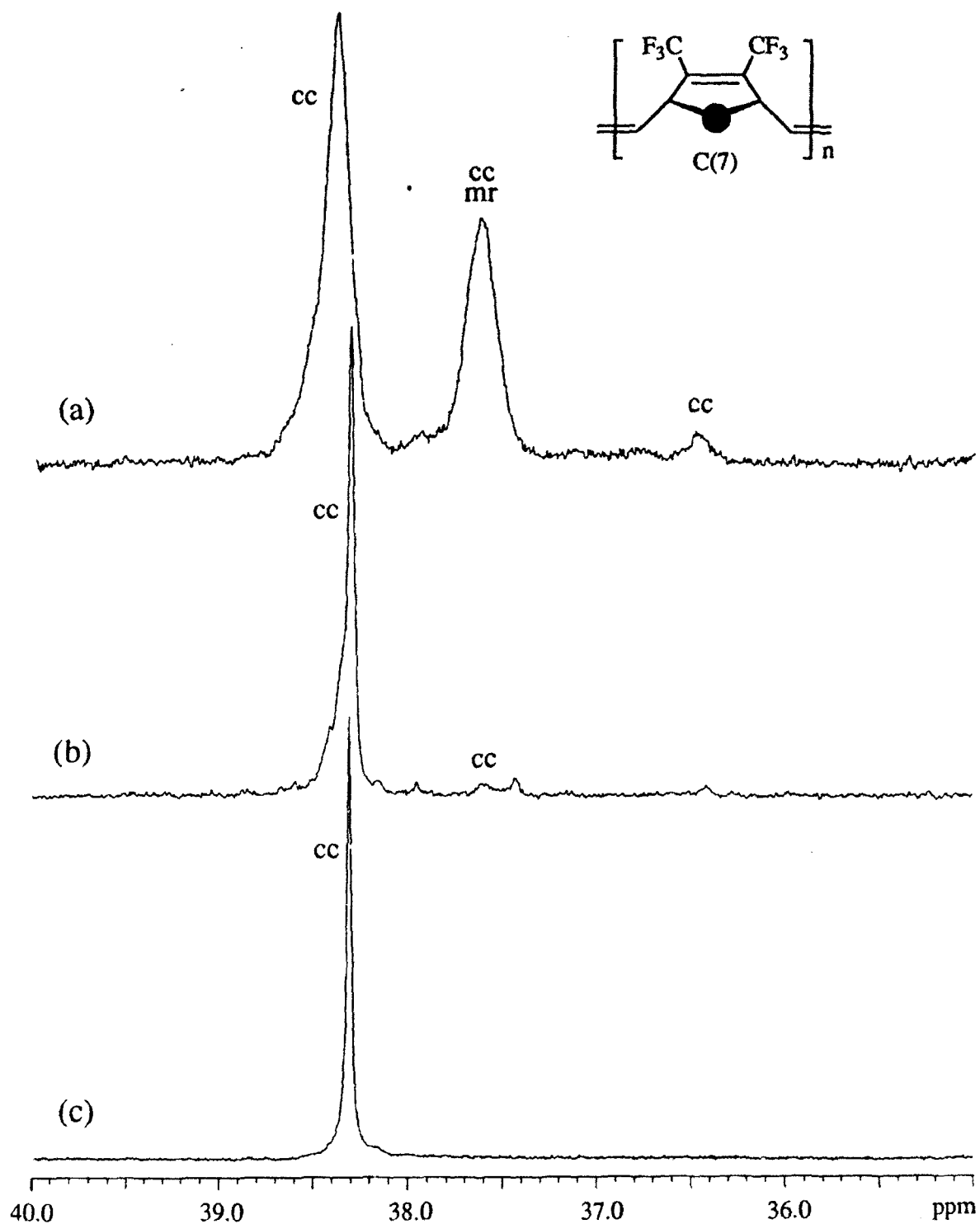


Figure 1. The C(7) region of the 125.69 MHz  $^{13}\text{C}$  NMR spectrum in acetone- $d_6$  of polyNBDF6 prepared with initiator (a)  $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$ ; (b) (+)-2; and (c) ( $\pm$ )-4.

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